

# AT ENTERPRISES AND INSTITUTES

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## GLASS VESSELS FOR SMALL-TONNAGE PRODUCTION OF OPTICAL GLASS

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The materials of glass vessels for making glass produced by different manufacturers are investigated. Conclusions concerning the reasons for fracturing of the vessels are drawn on the basis of data from dilatometric analysis as well as optical and electronic microscopy.

**Key words:** glass vessels, glassmaking, quartz ceramic, microstructure of ceramic.

In the market for optical glass considerable attention is now being devoted to quality as well as expanding the assortment of glasses produced in small quantities. The existing technologies aimed at mass production of a limited number of sorts of glass cannot meet these requirements. In this connection small-tonnage technologies making it possible to produce small volumes of high-quality glass of different sorts are being adopted at the Lytkarino Optical Glass Works (LZOS). The development of small-tonnage technologies can be based on the use of electric pot furnaces. The size of the furnace and the type of heating elements, which support the maximum pot size and the maximum working temperature, respectively, are determined on the basis of the purpose of the furnace. The pot size in the small-size electric glass setups (furnaces) adopted at LZOS ranges from 30 to 80 liters and the maximum working temperature is 1500–700°C.

When using such a setup high glass quality is attained by, among other things, automating the temperature regime for making glass as well as by using mixing operations.

An important part of successful mastery of glassmaking technology are glass vessels, which must be highly resistant to a quite wide range of compositions in order to support high glass quality as well as to possess adequate heat resistance (capability to withstand an adequate number of thermal cycles, i.e., the maximum number of conversions).

The maximum number of thermal cycles with heating to 1300°C followed by cooling in water (water temperature

5–25°C) is obtained by using fireclay (10–25 thermal cycles) and high-alumina (15–20) refractories compared with dinas and periclase refractories (1–2).

One of the main types of ceramic vessels used in glassmaking at LZOS are fireclay crucibles produced in-house by means of hydrostatic pressing (Fig. 1).

The average convertibility of fireclay crucibles ranges from one to eight depending on the composition of the glass. The maximum operating temperature of fireclay crucibles is 1580°C, above which the pot material dissolves and so-called nodal platted defects form. This long-time problem of the enterprise that is characteristic for making glass with ‘crown’ compositions is solved by finding the optimal ratio of the parameters temperature – melting time – mixing time for each composition individually as well as by using special coatings on the inner surface of the pot in order to increase the stability of the glass. However, if there are special requirements for the light transmission of the glass and inclusions of different nature, then it is impossible to obtain high quality. This pertains first and foremost to glass for fiber optics, such as VO-67 (refractive index  $n_e = 1.49$ ), which is used for tubes paired with rods made of TBF10IM high-index glass ( $n_e = 1.79$ ). These tubes are used for drawing out rigid light guides in the production of fiber-optic plates and elements that rotate an image by 180°.

To master glassmaking in small-size furnaces, among the ceramic crucibles, made of aluminum-silicate materials and pure oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{ZrO}_2$ ), used for melting optical glass the use of quartz ceramic is most prevalent and promising. Ceramic based on pure silicon dioxide is stable

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**Fig. 1.** Ceramic vessel produced at LZOS.

against most compositions of optical and special technical glasses with silicate as well as phosphate binder. In addition, quartz ceramic differs from other types of ceramic by its small linear thermal expansion coefficient (CLTE) and high heat resistance [1 – 4]. Pure silicon dioxide is a component of the most widely used optical glasses, and for this reason its negligible amounts migrating from the crucible material into glass can be corrected so that the glass composition will correspond to the prescribed one.

For higher-temperature compositions with fining temperature of the molten glass exceeding 1600°C materials with a high content of alumina (corundum, mullite-corundum) are promising for making crucibles.

Vessels made mainly of quartz ceramic are used in the process of mastering small-tonnage technology for the production of optical and special technical glasses. The present work analyzes the operation of glass vessels made from quartz ceramic (stekrit) manufactured by three producers (Nos. 1, 2 and 3). Samples were taken from different parts of the vessels before and after operation to investigate the composition and structure of the vessels made of quartz ceramic.

The phase composition was studied by the immersion method in a Polam R-211 polarization microscope using the HCAM 439-PC procedure, which makes it possible to obtain category-3 specimens. Dilatometric studies of the material for the purpose of determining its behavior during heating and cooling were conducted on 4 × 6 × 25 rectangular samples in a NETZSCH DIL 402PC dilatometer. A Vega 3 scanning electron microscope (Tescan Company) with a cathode made of lanthanum hexaborate LaB<sub>6</sub> was used for the microscopic studies in a high-vacuum regime. A thin layer of carbon (up to 15 nm thick) was deposited beforehand on non-conducting samples. The photography was performed using secondary electron detectors (SE) with accelerating voltage 5 – 10 kV.

In the course of the tests batches of vessels from different producers showed different stability against heating – melting – cooling, which was termed convertibility (Table 1).

**TABLE 1.** Convertibility and Linear Thermal Expansion Coefficient of Vessels from Different Manufacturers

Capacity	Convertibility	CLTE, 10 <sup>-6</sup> K <sup>-1</sup> , at 20 – 600°C
No. 1	3	1.1
No. 2	1	1.3
No. 3	1	1.4

**TABLE 2.** Structure of the Materials of Glass Vessels from Different Manufacturers

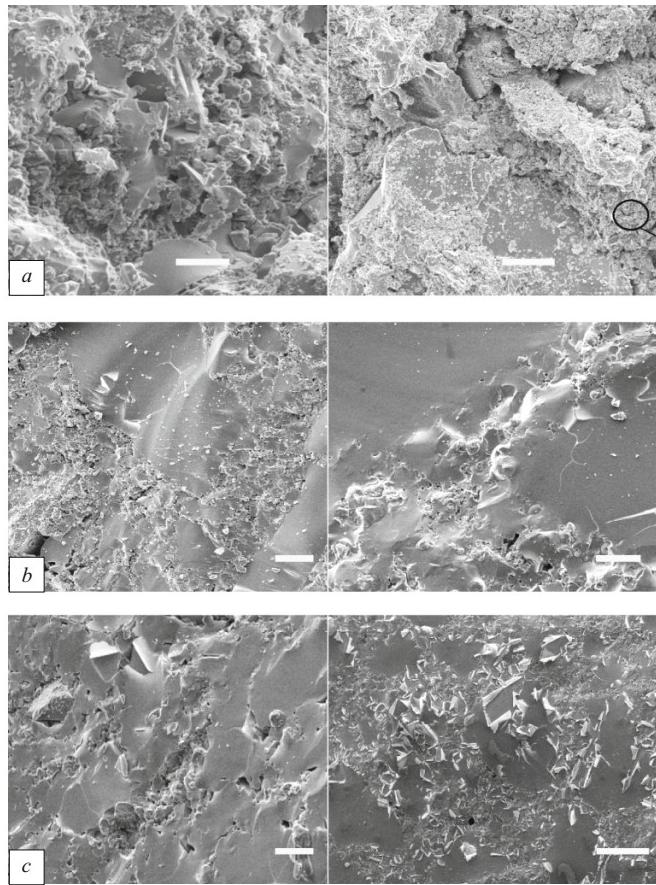
Manufacturer	Main phases	Fractional composition of quartz sand grains	
		Size, mm	Mass fraction, %
No. 1	Quartz glass, metacristobalite, tridomite, pseudowollastonite	1.0 – 2.5 0.05 – 0.1 < 0.01	30 – 35 15 50 – 55
No. 2	Quartz glass, metacristobalite, tridomite, quartz	2.5 – 5.0 0.5 – 1.5 < 0.025	60 – 65 25 – 30 10 – 15
No. 3	Quartz glass, metacristobalite, tridomite, pseudowollastonite	0.5 – 1.0 0.1 – 0.2 < 0.005	25 – 30 55 – 60 10 – 15

An investigation of the microstructure of the samples showed that the materials of the vessels from different manufacturers have much in common but there are visible differences also (Table 2).

#### INITIAL MICROSTRUCTURE OF THE MATERIALS OF GLASS VESSELS OBTAINED FROM DIFFERENT MANUFACTURERS

*Glass vessel from manufacturer No. 1.* The main phase of vessel material (Fig. 2a) consists of quartz glass in the form of angular and slightly rounded grains 2.5 – 1.0 mm in size. The grains of quartz glass contain a significant amount of gaseous inclusions 3 – 15 µm in size. The cementing phase consists of individual fine grains of quartz glass up to 0.06 mm in size, metastable outwardly structureless cristobalite, tridomite and pseudowollastonite  $\alpha\text{-CaO} \cdot \text{SiO}_2$  nuclei in the form of thin films on tridomite crystals (Fig. 2a). The grains of quartz sand are loosely cemented by a binding phase, and intermittent cracks are observed around them. The fracture is uneven; protruding grains of quartz glass or traces of their punctures are visible on them.

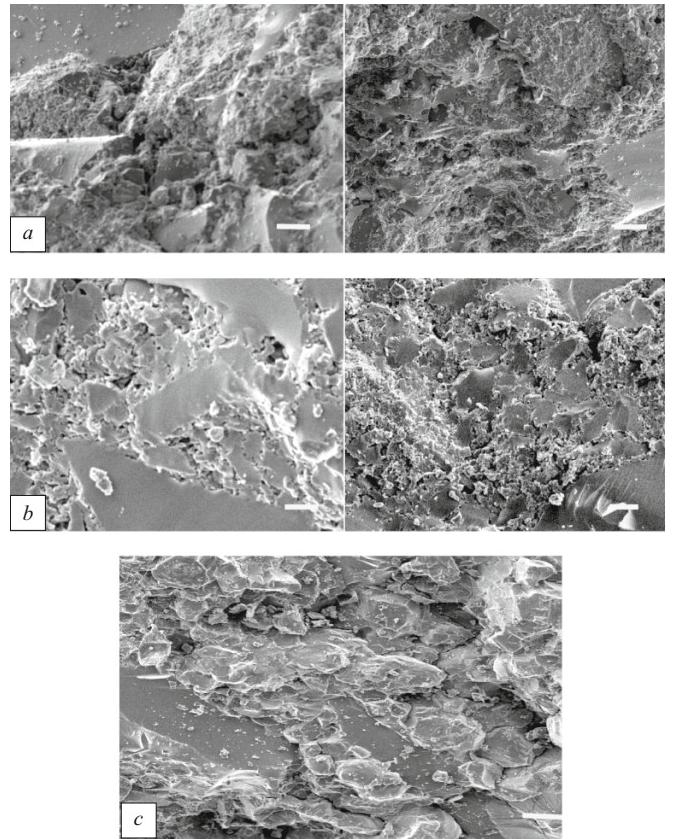
*Glass vessel from manufacturer No. 2.* The vessel material possesses a relatively simple microstructure, represented by different modifications of silica (Fig. 2b). The main phase of the material consists of quartz glass in the form of



**Fig. 2.** Microstructure of the material of glass vessels before use: *a*) manufacturer No. 1; *b*) manufacturer No. 2; *c*) manufacturer No. 3.

slightly rounded, colorless, transparent grains 0.5 – 1.0 mm in size. The binding phase consists of fine tridomite crystals forming concretions up to 5  $\mu\text{m}$  in size in some locations, metacristobalite in the form of dendritic aggregates consisting of a trunk from which small branches protrude at angles 45 – 90° with an octahedral head and amoeboid pseudowollastonite formations (see Fig. 2*b*). The grains of quartz sand are tightly cemented by the binding mass, and the fracture is even and occurs along the binding mass as well as the quartz grains.

*Glass vessel from manufacture No. 3.* The vessel material consists of large, somewhat elongated, irregular grains of fused quartz (Fig. 2*c*). The quartz grains are covered by a network of cracks filled with metacristobalite. Small needles and lance-like tridomite twins forming concretions containing glass are distributed around the quartz grains (see Fig. 2*c*). The material is permeated by closed rounded pores and contains a significant amount of black carbon impurities. A binder mass of the same color as the grains of fused quartz is present on the fracture. The quartz grains are tightly cemented; the fracture is even and passes along the binding mass as well as the grains of fused quartz.



**Fig. 3.** Post-use microstructure of the material of glass vessels: *a*) manufacturer No. 1; *b*) manufacturer No. 2; *c*) manufacturer No. 3.

#### POST-USE MICROSTRUCTURE OF MATERIALS OF GLASS VESSELS FROM DIFFERENT MANUFACTURERS

During use the materials of all vessels are exposed to high temperatures and, which is very important, large temperature differences. As a result of such exposure the microstructure of the materials of all vessels possesses a zonal structure characteristic for silica grains subjected to polymorphous transformations (Fig. 3) [5].

*Glass vessel from manufacturer No. 1.* During use the vessel material is subjected to high temperature and a temperature differential. As a result a zonal structure arises in it. The least altered zone is structurally almost identical to the vessel material before use. The characteristic angular fragments consist of partially cristobalitized quartz glass with traces of tridomite and pseudowollastonite. The crystallization of tridomite is more distinct in the transitional zone. The shapes of these segregations are prisms, forming concretions, and the amount of the amorphous glass increases. The structure becomes denser, and cracks are filled with a glassy material, which binds the fine crystals of the cementing mass, forming a dense monolithic structure (Fig. 3*a*).

*Glass vessel from manufacturer No. 2.* During use the material acquires a zonal structure. Cristobalite and tridomite zones form along the temperature gradient. The crystals in the cristobalite and tridomite zones are not directly connected. The tridomite zone consists of densely interleaved, short-prismatic and plate-shaped tridomite crystals. Segregations of calcium and iron silicates in the form of intermittent interlayers are observed in large quantities between the tridomite crystals. The cristobalite zone consists of anisotropic flaky cristobalite, forming sections of rounded, sometimes elongated shape ranging in size from 0.06 to 0.3 mm. The sections consist of isometric flakes, seemingly superposed on one another, ranging in size from 0.005 to 0.01 mm and bordered by a very thin glassy film. Such sections are tightly packed against one another in some cases and accumulations of pores between them are observed in other cases (Fig. 3b).

*Glass vessel from manufacturer No. 3.* During use only the tridomite zone forms in the vessel material. It consists of a large amount of quite large tridomite crystals ranging in size from 0.04 to 0.1 mm, forming concretions with one another. The gaps between them are filled with glassy material. Dendritic segregations of pseudowollastonite, evidently forming from the glassy material, are observed in large quantities (Fig. 3c).

Dilatometric studies of samples from manufacturer No. 1 showed that they undergo significant additional shrinkage as a result of sintering of the material. No significant volume effects were observed during heating and cooling. Evidently, this is associated with the compensation of the volume changes during polymorphic transformations by processes occurring in the second phase of the material — the aluminum-silicate binder.

Dilatometric studies performed on samples of vessel materials showed practically identical values of the CLTE in the temperature range 20 – 600°C. In addition, sharp expansion of the material is observed at temperatures 230 – 240°C. This is explained by a polymorphic transformation of cristobalite from  $\alpha$ - into the  $\beta$ -modification. The transition can result in the appearance of microcracks and premature failure of the crucible material. The polymorphic transformation is especially distinct at the indicated temperatures in samples of the material from manufacturer No. 2.

To determine the amount of cristobalite leading ultimately to failure of the material we used the method described in [6].

The content of cristobalite was evaluated using the equation

$$K = \frac{\Delta l}{1.05} \times 100\%,$$

where  $\Delta l$  is the linear expansion (%) determined from a plot and the factor 1.05 is the magnitude of the indicated effect for pure cristobalite.

According to the evaluation made above, the amount of cristobalite formed as a result of firing in the crucible from manufacturer No. 1 is approximately a factor of 3 smaller than in the crucibles from the manufacturers Nos. 2 and 3.

## ANALYSIS AND CONCLUSIONS

The data from petrographic analysis confirmed the initial idea that the polyfractional composition of the material could be useful, affording density and stability at elevated temperatures [7].

The phase compositions of the materials studied were similar to one another and contained different fractions of quartz glass and silicate binder, even though there were significant differences in the microstructure.

Dilatometric studies showed that on the whole the material from the manufacturer No. 1 is more stable on heating against volume changes because of  $\text{SiO}_2$  polymorphism and its CLTE is smaller than in the material from the manufacturer No. 2. In our opinion this effect was achieved by means of the phase composition of the material containing as binder a high-alumina phase affording high glass stability of the crucible as well as low heat-treatment temperature of crucibles that is insufficient for complete sintering of the material, which increased the heat resistance of the material.

It is known that the most common reason for failure of articles based on silica which are subjected to heating and cooling cycles is the formation of microcracks as a result of polymorphic transformations of modifications such as quartz and cristobalite. The prevention of polymorphic transformations is a difficult problem and reduces either to using ultrapure quartz glass as the initial material or stabilizing the structure by inserting into the crystalline structure modifications of ions preventing polymorphism. It should be noted that it is practically impossible to prevent the crystallization of quartz glass during repeated heating and cooling cycles: any impurity ions under these conditions serve as nuclei for crystallization, which starts first from the outer surface of the articles.

This process can only be slowed down and an attempt can be made to create a microstructure of the material in which the formation of microcracks does not lead to their expansion and development. This can be done using grains of relatively inert material, such as unique fireclay — corundum, mullite, sillimanite as well as a specially created imperfect structure of incompletely sintered material. In the first case a microcracked heat-resistant structure in which polymorphic transformations will not lead to the development of macrocracks will be formed. In the second case the formation of cracks will be stopped by the presence of empty space between the grains of sintered material.

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